G-33-633 Postal

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: May 20, 1971

Project Title: Nuclear Magnetic Resonance Relaxation

Project No: B-1598 (Term. as G-33-633)

Principal Investigator: Dr. Sidney L. Gordon

Sponsor: National Science Foundation

Agreement Period: From June 1, 1971 Until May 31, 1973

Type Agreement: Grant No. GP-28921

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$36,400 NSF Funds (B-1598)
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Sponsor Contact Person (s):
O. William Adams
Program Director for Structural Chemistry
National Science Foundation
Washington, D.C. 20550

Continuation of Project B-1543.

Assigned to: School of Chemistry

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RA-3 (2-71)

GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

Date: September 26, 1974

Project Title: Nuclear Magnetic Resonance Relaxation

Project No: G-33-633 (formerly B-1598)

Principal Investigator: Dr. S. L. Gordon

Sponsor: National Science Foundation

Effective Termination Date: 5-31-74

Clearance of Accounting Charges: by 5-31-74

Grant Closeout Actions Remaining: Final Fiscal Report
(Office of Financial Affairs)

Assigned to School of Chemistry

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Terminated Project File No. _____
Other _____

Georgia Institute of Technology
Atlanta, Georgia 30332

June 1, 1972

First Annual Report for

NSF Grant GP-28921

NUCLEAR MAGNETIC RESONANCE RELAXATION

Prepared for the

National Science Foundation

by

Sidney L. Gordon
Associate Professor of Chemistry

This research program is concerned with the detailed characterization of nuclear spin relaxation in liquids and gases. The research carried out with the aid of this grant will be described under the following headings:

A. Overhauser Studies in Three Spin Systems
B. Relaxation Time Studies in Halogenated Methanes
C. Intermolecular Contribution to Proton Relaxation

A. Overhauser Studies in Three Spin Systems

Dr. Ping Yang developed a formalism to describe Overhauser experiments in three-spin systems.[1,2] In this formalism, theory and experiment are compared using the relative fractional intensity changes $G_{ab,cd}$, where

$$G_{ab,cd} = F_{ab,cd} / F_{cd,cd}$$

and $F_{ab,cd}$ is the fractional intensity change in line ab when line cd is irradiated. Although $F_{cd,cd}$ cannot be observed directly, it can be computed indirectly using the summation rules,

$$\sum_{(ij)} F_{ij,cd} = 0$$

where summation involves any closed path on the energy level diagram. Dr. N. R. Krishna has cast the theory for weakly coupled spin systems in terms of geometrical figures which display the symmetry of the system.[3] He has compared theory with experiment for two three-spin systems: the ABX system vinyl bromide, and the AX_2 system 1,1,2 - trichloroethane. Dr. Krishna found that he could obtain accurate values of the relative contributions for inter and intramolecular contributions to proton relaxation by comparing the experimental and theoretical $G_{ab,cd}$.

B. Relaxation Time Studies in Halogenated Methanes

Mr. Patrick Brown is measuring the T_1 and T_2 relaxation times of halogenated methanes as a function of concentration in the non-magnetic solvent CS_2.[4] The data is being extrapolated to infinite dilution. The extrapolated relaxation times are being interpreted in terms of two mechanisms: internal dipolar interactions, and scaler coupling between proton and halogen nuclei. The results will be used to study the reorientational motion of these molecules. This study is an extension of Dr. Charles Miller's work on the chlorinated ethanes.[5,6] The methane derivatives used here have rigid structures in contrast to the halogenated ethanes which have the possibility of internal rotation. This allows a more straight forward comparison of the experimental results with theory.

C. Intermolecular Contribution to Proton Relaxation in Liquids

Dr. N. R. Krishna is studying intermolecular dipolar interactions in liquids. The model of external isotropic random fields is often used to approximate intermolecular dipolar interactions while studying relaxation processes in coupled nuclear spin systems in high resolution NMR. In systems where the random fields are entirely due to intermolecular dipolar interactions, a comparison of the strength of the random field at different nuclear sites would yield information about the strength of intermolecular interactions at different nuclei. Dr. Krishna is evaluating the strengths of these random fields using intramolecular Overhauser experiments and inversion - recovery curves.

Dr. Krishna is also studying the intermolecular dipolar interactions using intermolecular Overhauser experiments. In the intermolecular Overhauser experiment the intermolecular dipolar interactions, the ultimate source of the external random fields, is studied in detail. Dr. Krishna has developed a density matrix formalism to describe the intermolecular Overhauser experiment on coupled spin systems, and is testing its predictions on solutions of 1,1,2 - trichloroethane in cyclohexane.[7]

References

1. P. P. Yang, "Nuclear Spin Relaxation in Three Spin System," Ph.D. Thesis in Chemistry, Georgia Institute of Technology, 1972.

2. P. P. Yang, "Overhauser Studies in Three-Spin Systems," Third South eastern Magnetic Resonance Conference, Oak Ridge, Tennessee, Oct. 21, 1972.

3. N. R. Krishna, P. P. Yang, and S. L. Gordon, "Overhauser Studies in Three-Spin Systems," (to be published).

4. P. M. Brown, "Nuclear Relaxation in Halogenated Methanes," Georgia Academy of Science Meeting, Athens, Georgia, April 29, 1972

5. C. R. Miller, "Nuclear Spin Relaxation in the Chloroethanes," Ph.D. Thesis in Chemistry, Georgia Institute of Technology, 1970.

6. C. R. Miller and S. L. Gordon, J. Chem. Phys. 53, 3531 (1970).

7. N. R. Krishna, "Intermolecular Overhauser Studies in Liquids," Georgia Academy of Science Meeting, Athens, Georgia, April 29, 1972.

Yale: G-33-633

Georgia Institute of Technology

Atlanta, Georgia 30332

August 1, 1974

Final Technical Report for

NSF Grant GP-28921

NUCLEAR MAGNETIC RELAXATION

STARTING DATE 6/1/71
COMPLETION DATE 5/31/74

Prepared for the

National Science Foundation

by

Sidney L. Gordon

Associate Professor of Chemistry

I. Publications

The following publications describe research carried out with the support of this grant:

1. N. R. Krishna and S. L. Gordon, Phys. Rev. A 6, 2059 (1972). "Fourier Transform for a Single Nucleus of Spin ½ in the Presence of a Strong rf Field".

2. N. R. Krishna, P. P. Yang, and S. L. Gordon, J. Chem. Phys. 58, 2906 (1973). "Selective Nuclear Overhauser Effect Experiments on Coupled Spin Systems."

3. N. R. Krishna and S. L. Gordon, J. Chem. Phys. 58, 5687 (1973). "Intermolecular Nuclear Overhauser Studies of Coupled Spin Systems in High Resolution NMR."

4. N. R. Krishna and S. L. Gordon, J. Chem. Phys. 59, 4569 (1973). "Intermolecular Nuclear Overhauser Effects in A_nB_n Spin Systems with Asymmetric Relaxation."

5. P. Brown, N. R. Krishna, and S. L. Gordon, "Proton Spin Relaxation in the Halogenated Methanes," Manuscript in preparation.

6. R. L. Harris and S. L. Gordon, "Intermolecular Overhauser Studies of proton - C^{13} Interactions," manuscript in preparation.

II. Personnel

The following students were collaborators in this research program.

1. Ping P. Yang, Ph. D. candidate in the School of Chemistry

2. Robert L. Harris, Jr., M. S. candidate in the School of Chemistry

3. Patrick M. Brown, B. S. Candidate in the School of Chemistry

4. Dr. N. R. Krishna, postdoctoral assistant.

Dr. Yang was supported by a research assistantship using funds from this grant. Dr. N. R. Krishna was supported by a postdoctoral research assistantship using funds from this grant. Mr. P. Brown was supported by a research assistantship during one summer using funds from this grant.

III. Theses

The following theses were written on research supported by this grant.

1. Ping P. Yang, "Nulcear Spin Relaxation in Three Spin Systems," Ph. D. dissertation, School of Chemistry, Georgia Institute of Technology, 1972.

2. Robert L. Harris, Jr., "Applications of Proton and Carbon-13 Nuclear Magnetic Resonance to the Study of Molecular Translation in Liquid Solution," M. S. dissertation, School of Chemistry, Georgia Institute of Technology, 1974.

IV. Description of Research

With the support from this grant, we have studied reorientational and translational motions of small molecules in liquid solution using proton dipolar relaxation. We have demonstrated that steady state weak irradiation double resonance using either the intramolecular or intermolecular nuclear Overhauser effect offers simple and sensitive procedures for isolating the intramolecular and intermolecular dipolar contributions to proton relaxation. A more detailed description of the research is given in the following.

A. Fourier Transform Double Resonance

Dr. N. R. Krishna carried out a density matrix analysis of the Fourier transform of the response to a $\pi/2$ pulse of a single nucleus of spin 1/2 interacting with a strong rf field. This is the basic Fourier transform double resonance experiment. It was shown that the resulting Fourier transform spectrum differs in intensities from the steady-state double resonance spectrum, in contrast with the usual single resonance case. This occurs because the nuclear spins are polarized in the rotating frame along a direction different from the laboratory z axis.

B. Selective Nuclear Overhauser Effect Experiments

Dr. P. P. Yang and Dr. N. R. Krishna developed a formalism describing selective nuclear Overhauser effect experiments on strongly coupled spin systems.[2, 3, 4] In these experiments, one line of an NMR spectrum is partially or totally saturated by a strong rf field. This causes the populations of all spin levels to change in a manner which depends up the relative magnitude of the various thermal transition probabilities. As a result, there occurs a change in the intensity of the other lines observed by simultaneously sweeping the frequency of the weak observing rf field. These steady state changes are referred to as the general nuclear Overhauser effect. In the selective nuclear Overhauser experiment, the strength of the saturating rf field is kept low enough so as not to cause double resonance splittings in the connected transitions. The double resonance spectrum may then be treated as single resonance spectrum with intensity changes reflecting the Overhauser effect. If one saturates successively each of the n different resonance lines of a spectrum, and observes simultaneously the intensities of all the other resonance lines, one is able to obtain n(n-1) data. Drs. Yang and Krishna formulated the theory in terms of the n(n-1) relative fractional intensity changes, $G_{ab,cd}$, where transition cd is irradiated and transition ab is observed. As a reference line for computing the $G_{ab,cd}$, the irradiated line, cd, itself was selected. Although the fractional intinsity change of the irradiated line cannot be directly observed, it may be computed from observable fractional changes using summation relations. The relative fractional intensity changes, defined in this way, have a universal character for any spin system. A comparison of computed and experimental values of $G_{ab,cd}$ provides a straightforward way of analyzing proton relaxation mechanisms in

coupled spin systems. For three-spin systems of the type A_2X and ABX, where the two A or AB spins are close and both distant from the X nucleus, it was shown that the particular experiment where the outer line of the X multiplet is saturated is quite sensitive to the detailed relaxation mechanism. The remaining lines of the X multiplet directly reflect the fractional contribution of the intramolecular dipole-dipole mechanism. The sensitivity of the experiment for the X-multiplet was clearly seen in the recorded spectra of the three-spin systems, 1, 1, 2-trichloroethane and vinyl bromide.

C. Intermolecular Nuclear Overhauser Effect Studies

Dr. Krishna developed a density matrix formalism for intermolecular nuclear Overhauser effect[5] experiments in high resolution NMR systems.[6, 7, 8] It was shown that the steady state intermolecular nuclear Overhauser effect experiment offers a sensitive technique for studying the internal relaxation mechanisms of a solute in dilute solution in a protonated solvent. In the steady state experiment, the solvent spins are saturated by a strong rf field, while the frequency sweep NMR spectrum of the solute is recorded. The equations, describing the steady state experiment, are formulated entirely in the spin space of the solute molecule. The solvent enters the equations only in terms of the spectral densities for the intermolecular dipolar interaction. The equations are straightforward to solve, and closed form solutions may be obtained for important simple cases. An important consequence of the equations is that, in the limit of infinite dilution, the Overhauser enhancement for each line in the high resolution NMR spectrum is $\gamma_S/(2\gamma_I)$, where γ_S and γ_I are the magnetogyric ratios for the solvent and solute spins, respectively. This result is true even for strongly coupled

spin systems with non-zero intermolecular dipolar correlation coefficients, provided the solute has no intramolecular relaxation mechanism. Thus, any deviation of the Overhauser enhancements from $\gamma_S/(2\gamma_I)$ is a measure of internal relaxation, and the intermolecular nuclear Overhauser effect experiment offers a teacnique complimentary to intramolecular double resonance for the analysis of relaxation in coupled spin systems. Dr. Krishna illustrated the technique by analyzing the relaxation of 1, 1, 2-trichloroethane in dilute solution in tetramethylsilane. The measured Overhauser enhancements allowed a detailed relaxation analysis in terms of intramolecular and intermolecular dipole-dipole interactions.

D. Proton Relaxation in the Halomethanes

Mr. P. M. Brown and Dr. N. R. Krishna measured the T_1 relaxation times for the various halomethanes as a function of concentration in CS_2.[9] The relaxations rates were extrapolated to infinite dilution in CS_2 in order to compare the reorientational motions in a common medium. The results were anomalous in that they contradicted the trends of analogous studies on the chloroethanes. Temperature dependent studies revealed a substantial amount of relaxation is due to the spin-rotation mechanism. When the room temperature results were corrected for the spin-rotation contributions, good agreement of experimental and theoretical relation times were obtained using an inertial model for reorientation.

E. Intermolecular Proton - C^{13} Dipolar Relaxation

Mr. Robert L. Harris obtained the intermolecular proton - C^{13} dipolar relaxation rates for solutions of acetone - D6 in water.[10] The dominant competing mechanism was the C^{13} spin-rotation interaction. The isolation of intermolecular

dipolar contribution was accomplished by combining nuclear Overhauser effect experiments with spin lattice relaxation time measurements. The results were used to study the specific association between the water molecules and the carbonyl group of the acetone.

References

1. N. R. Krishna and S. L. Gordon, "Fourier Transform for a Single Nucleus of Spin ½ in the Presence of a Strong rf Field," Phys. Rev. A, 6, 2059 (1972).

2. P. P. Yang, "Nuclear Spin Relaxation in Three Spin Systems," Ph. D. thesis in Chemistry, Georgia Institute of Technology, 1972.

3. P. P. Yang, N. R. Krishna and S. L. Gordon, "Overhauser Studies in Three-Spin Systems," 164th ACS National Meeting, New York, New York, August, 1972.

4. N. R. Krishna, P. P. Yang, and S. L. Gordon, Selective Nuclear Overhauser Effect Experiments on Coupled Spin Systems," J. Chem. Phys. 58, 2906 (1973).

5. R. Kaiser, J. Chem. Phys. 42, 1838 (1965).

6. N. R. Krishna and S. L. Gordon, "Intermolecular Overhauser Studies of Coupled Spin Systems in Liquids," 164th ACS National Meeting, New York, New York, August, 1972.

7. N. R. Krishna and S. L. Gordon, "Intermolecular Overhauser Studies of Coupled Spin Systems in High Resolution NMR," J. Chem. Phys. 58, 5687 (1973).

8. N. R. Krishna and S. L. Gordon, "Intermolecular Nuclear Overhauser Effects in $A_n B_n$ Spin Systems with Asymmetric Relaxation," J. Chem. Phys. 59, 4569 (1973).

9. P. M. Brown, N. R. Krishna, and S. L. Gordon, "Nuclear Spin Relaxation in Halogenated Methanes," Fifth International Symposium on Magnetic Resonance, Bombay, India, January, 1974.

10. R. L. Harris, Jr., "Applications of Proton and Carbon-13 Nuclear Magnetic Resonance to the Study of Molecular Translation in Liquid Solution," M. S. Thesis in Chemistry, Georgia Institute of Technology, 1974.